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Field evaluation of a mobile high-capacity particle size classifier (HCPSC) for separate collection of coarse, fine and ultrafine particles

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Abstract

This paper presents results from a field evaluation of a mobile high-capacity particle size classifier (HCPSC) which samples at 850 l min^{-1} and classifies ambient particles in three size groups: coarse, fine (or accumulation) and ultrafine modes. Particles in coarse and fine modes are collected by impaction on a small, uncoated surface area (14 cm^2) and can be extracted with a small amount of solvent for toxicological tests and chemical characterization. Particle bounce is eliminated by using cavity-type impaction substrate configurations. Polyurethane foam is used as the impaction substrate material. Ultrafine particles are collected on $20 \times 25 \text{ cm}$ quartz or Teflon filtersTM (PTFE). The performance of the HCPSC was evaluated in a field study conducted in the Netherlands from May to August 1999. Field tests showed that mass, chloride, nitrate and sulfate concentrations in the coarse mode ($2.5\text{--}10 \mu\text{m}$) measured by means of the HCPSC and a collocated Micro-Orifice Uniform Deposited Impactor (MOUDI) were in very good agreement (within 10% or less). Comparison between fine mode PM concentrations obtained with the HCPSC and MOUDI indicated that approximately 10–15% of fine mode particles are carried over to the ultrafine mode due to imperfect collection efficiency characteristics of rectangular geometry impactors (HCPSC) compared to round nozzle impactors (MOUDI). Comparisons between the PM-2.5 nitrate concentrations obtained with the HCPSC and MOUDI and those with a collocated Harvard/EPA Annular Denuder Sampler (HEADS) yielded average nitrate sampling efficiencies of about 80 and 70% for HCPSC and MOUDI, respectively. Nitrate losses from Teflon filters during this study were on the average higher than 50%. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: High-volume sampler; Particle size classification; Coarse fine and ultrafine PM; Toxicity test

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1. Introduction

Epidemiological evidence associating ambient particulate pollution with adverse health effects in humans is extensive (American Thoracic Society, 1996; Environmental Protection Agency, 1996). Nevertheless, fundamental uncertainty and disagreement persist regarding what physical and chemical properties of particles (or unidentified confounding environmental influences) can influence health risks, what pathophysiological mechanisms are operative, and what air quality regulations should be adopted to deal with the health risks.

The recent development of ambient particle concentrators (Sioutas, Koutrakis & Burton, 1995a; Sioutas, Wolfson, Ozkaynak & Koutrakis, 1997a, Sioutas et al., 1997b, 1999) has made it possible to perform laboratory exposures with “real-life” ambient aerosols at increased (but still realistic) concentrations. Initial results showed increased toxic responses to concentrated particles (Gavett et al., 1999; Godleski, Sioutas, Katler & Koutrakis, 1998; Clarke et al., 1999), thereby suggesting that this type of exposure system may provide a useful method for assessing the health effects of ambient particles.

Particle size and composition are two very important parameters in determining particle toxicity. There is a great need for PM toxicity studies that target specific chemical and/or physical PM properties, in their “real-life” state and at realistic levels. Such data are needed to address many of the most important air pollution-related health problems, including the exacerbation of asthma, respiratory- and cardio-vascular disease, and the role of particulate matter in human mortality. Particle chemical composition varies from location to location. Even at the same location, chemical compositions will largely depend on weather conditions, i.e. wind direction, temperature and relative humidity, which change from day to day (or even within a day). It is therefore difficult to replicate and/or control the chemical composition of the atmosphere of an exposure study that uses concentrated real-time ambient particles.

Alternative approaches in determining the toxicological potential of ambient PM include intratracheal instillation and in vitro studies. These techniques have the advantage of being simpler, as they do not require the expertise and expense involved in inhalation exposures. Useful toxicological information can be obtained of a single dose of known (and often controllable) quantity and chemical compositions of particles (Amdur, 1996). Both of these techniques can therefore compliment inhalation and generate valuable information on assessing relative PM toxicity.

This paper presents results from the performance evaluation of a mobile high-capacity particle size classifier (HCPSC) which was used to collect different PM fractions for in vitro and intratracheal instillation toxicological studies. The HCPSC operates at a sampling flow rate of 850 l min^{-1} and is designed to classify ambient PM in three size groups: coarse, fine and ultrafine particles. Along with its originally intended use in toxicological studies, the HCPSC presented here can also be used to determine the physicochemical profiles of ambient PM at different locations in a relatively short time (i.e., within few hours) due to its high sampling flow rate.

2. Methods

2.1. Description of the three-stage HCPSC

The HCPSC, shown in Fig. 1, consists of three parts: (1) a modified version of the high-volume TE-6001 size selective inlet (SSI) PM_{10} inlet (Tisch Environmental Inc, Cleves, OH), (2) a

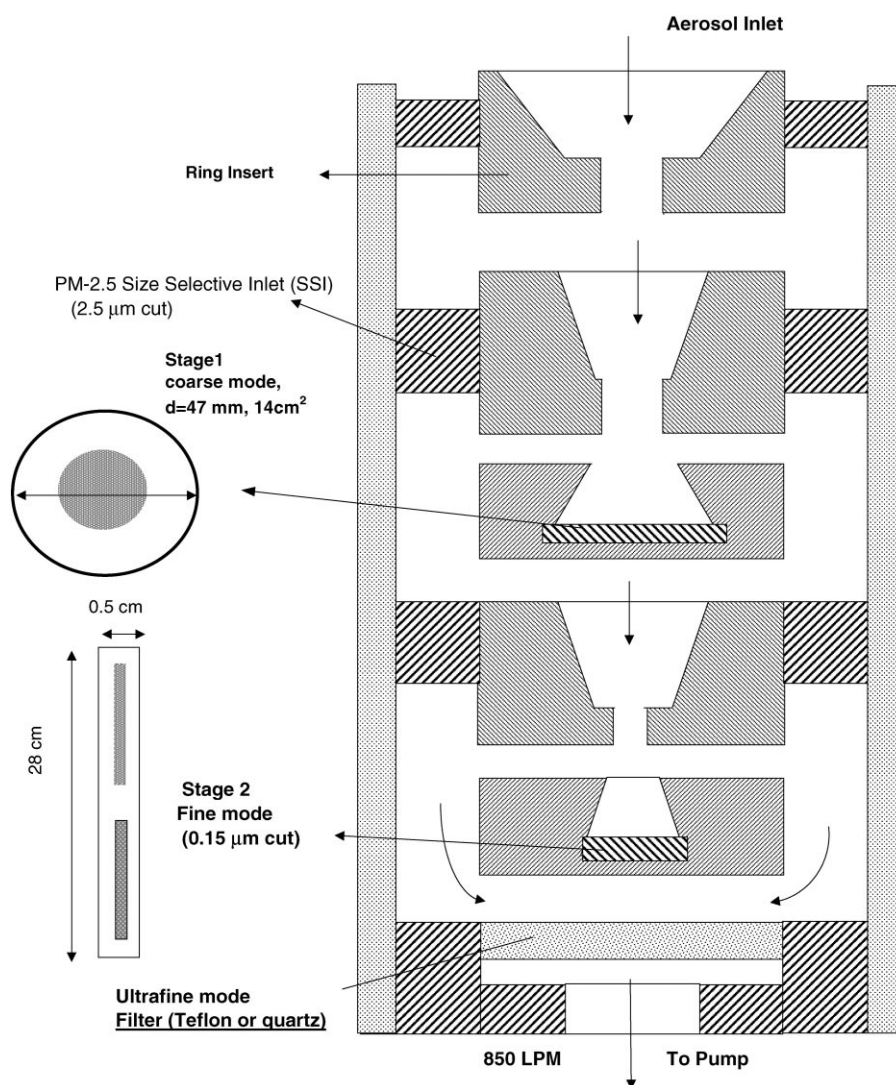


Fig. 1. Schematic of the high-capacity particle size classifier (HCPSC).

conventional high-volume slit impactor (HVSII), (Sioutas et al., 1997; Kavouras, Ferguson, Wolfson & Koutrakis, 2000) and (3) an filter holder with a filter substrate to collect ultrafine PM.

Ambient aerosols are drawn at an intake of 850 l min^{-1} through an aluminum inlet port, 5.5 cm long and 2.2 cm in diameter in SSI. An aluminum ring, 1.6 cm in diameter, is placed at the inlet of the acceleration nozzle. The flow contraction generated by the insertion of the aluminum ring causes particles larger than approximately $10 \mu\text{m}$ to deposit on the lip of the contraction. The design of this ring has been based on the experimental and numerical work by Muyshondt, McFarland and Anand (1996) and Chen and Pui (1995) on particle deposition in abrupt (i.e., 90° angle) pipe contractions. The relationship between the fraction of particles depositing on the walls

of the contracted part and particle aerodynamic diameter resembles that of conventional impactors. Particle deposition on the contraction can be predicted by means of the product $St(1 - A_o/A_i)$, where St is a modified Stokes number, defined as

$$St = \frac{\rho_p U_i d_p^2 C_p}{9\mu d_o}, \quad (1)$$

where d_p , ρ_p , C_p are the particle diameter, density and slip correction, μ is the air viscosity, U_i is the velocity at the inlet of the contraction and d_o is the diameter of the contraction. A_o and A_i are the areas of the ring and the inlet tube, respectively. The above dimensions of the contraction (e.g., ring) were chosen to yield 50% removal efficiency of 10 μm particles at a flow rate of 850 l min^{-1} through the ring.

Typically, impaction substrates are coated with an adhesive material to avoid particle bounce, which may be particularly pronounced at high jet velocities such as those in the SSI of HCPSC (i.e., approximately 44 m s^{-1}). However, the use of adhesive material is highly undesirable for both chemical analysis as well as toxicological studies using the collected particles. In order to avoid the use of adhesive coatings, coarse PM were collected on substrate within a thin hollow aluminum disk, 5 cm in diameter, placed at a distance of about 2.8 cm away from the exit of the acceleration nozzle. A conical cavity with an opening of 4.7 cm was formed by inserting a hollow aluminum ring to the existing substrate (shown schematically in Fig. 1). This impaction substrate design was based on a recent study (Chang, Kim & Sioutas, 1999) which has shown that this configuration results in collection efficiencies exceeding 90% for particles up to 10 μm , even without the use of coating. The dimensions of the bottom of the cavity substrate were chosen so that standard 4.7 cm filters, such as TeflonTM (PTFE), glass fiber or quartz filters, can be used for particle collection.

Particles smaller than 2.5 μm are drawn and accelerated through a rectangular slit conventional impactor with an acceleration nozzle 28 cm long and 0.033 cm wide. Particles larger than approximately 0.15 μm are collected on a narrow substrate, 28 cm long and 0.64 cm wide. The original design and experimental characterization of slit impactor is described by Sioutas et al. (1997). A modified version, using PUF instead of the original FluoroporeTM membrane as the impaction substrate is described by Kavouras et al. (2000). Finally, ultrafine particles (smaller than 0.15 μm) are collected on either a 20 \times 25.4 cm PTFE filter sheet (5 μm , Membrane filter, Schleicher & Schuell, Germany) or on 20 \times 25.4 cm quartz sheets (Pallflex Corp., Putnam, CT). PTFE, quartz and polyurethane foam (PUF, density 0.019 g/cm^3 , Merryweather Foam, Barberton, OH) were tested as the impaction substrates to collect coarse and fine PM. Although all of the aforementioned substrate materials were found suitable in terms of eliminating particle bounce (Chang, Sioutas, Kim, Gong & Linn, 2000), polyurethane foams were used in the field tests described in this work, due to their high loading capacity, low impurity content and inexpensive cost.

2.2. Field tests

A Micro-Orifice Uniform Deposited Impactor (MOUDI, MSP Corporation, Minneapolis, MN), and a Harvard/EPA Annular Denuder System (HEADS) sampled in collocation with the HCPSC and were used as reference samplers. The MOUDI sampled at 30 l min^{-1} and five stages were used to classify particles in the following aerodynamic diameter ranges: ≤ 0.16 , 0.16–1.8, 1.8–3.2, 3.2–10.0, and 10.0–18.0 μm . A 37 mm PTFE filter (2 μm , PTFE, Gelman, Ann Arbor, MI)



Fig. 2. Field sampling locations in the Netherlands from April 29th–July 27th 1999.

was used as the back up MOUDI filter to collect particles smaller than less than $0.16 \mu\text{m}$, whereas 47 mm PTFE filters were used as impaction substrates in all other MOUDI stages. The HEADS (Koutrakis, Wolfson, Slater, Brauer & Spengler, 1988) sampled at 101 min^{-1} , and consisted of an impactor inlet that removes coarse particles ($d_p \geq 2.1 \mu\text{m}$), followed by an annular denuder coated

with sodium carbonate to remove acidic gases. The filter pack has a 47 mm PTFE Teflon filter to collect fine particles and a 47 mm sodium carbonate coated glass fiber filter (2 μm , Gelman, Ann Arbor, MI) to collect volatilized particulate nitrate. The total nitrate collected in both PTFE and coated glass fiber filters yields the actual ambient particulate nitrate concentration. The sampling flow rates of MOUDI, HEADS and HCPSC were measured with calibrated flowmeters (Matheson, VWR Brand, Catalogue #61016-208 for MOI and HEADS; Kings Instrument, CA #7205-0171-A for HCPSC).

The performance of the HCPSC was initially evaluated at the premises of the National Institute of Public Health and the Environment of the Netherlands (RIVM) in Bilthoven between April 29 and May 30, 1999. Sampling periods varied from 4 to 12 h depending on the observed PM level. To determine particle mass concentrations, the PTFE filters of the MOUDI and the 4.7 cm PUF substrate (collecting coarse PM) of the HCPSC were pre-weighed and post-weighed using a Sartorius MC 5 microbalance (Sartorius, Gettingen, Germany), in a room with controlled temperature of 21–24°, and relative humidity of 40–50%. Post-weighing was conducted after a 48 h equilibration. Mass concentrations were only determined for the coarse PM fraction of the HCPSC because the PUF strip substrate (collecting 0.15–2.5 μm) and PTFE sheet (collecting ultrafine PM) could not be conveniently weighed due their shape and size.

For the analysis for ultrafine particles, a 4 cm \times 4 cm piece of the Teflon or quartz sheets was used, whereas the rest of the sheet was also used for in vitro toxicity studies. Before each experiment, the polyurethane foams were washed and sonicated with deionized water for 30 min twice, rinsed with ethanol and then covered with clean paper sheet in fume hoods for at least 24 h. At the end of each run, the polyurethane foam substrates of the HCPSC as well as the 3.7-cm Teflon filters of the MOUDI and the 4.7 cm Teflon filter and glass fiber filters of the HEADS were extracted with a solution of ethanol and ultrapure water. Ethanol was used in order to wet the hydrophobic Teflon and polyurethane filters. To extract the 4.7 and 3.7 cm Teflon filters 0.15 ml ethanol in 5 ml ultrapure water was used, whereas 3 ml ethanol in 14 ml ultrapure water was used for the polyurethane foam substrates and 4 cm \times 4 cm Teflon sheet of the HCPSC. Subsequently, the filters were sonicated for 15 min and analyzed for chloride, sulfate and nitrate ions by means of ion chromatography. The limit of detection (LOD) of chloride, nitrate and sulfate are 3.0, 2.0, 1.0 $\mu\text{mol l}^{-1}$, respectively.

The HCPSC was subsequently installed in a mobile trailer and was deployed to five different locations in the Netherlands (Fig. 2 and Table 1). These locations are affected by different emission

Table 1
Field study locations and PM sources

Location	PM sources
REMU	Utrecht city background, heavy freeway traffic, light industrial activities from west of Utrecht
Koningsbruggen	Utrecht city background, heavy freeway traffic
RCA (Amsterdam)	Dominated by dense local traffic emission
De Zilk	Background coastal area with smaller contribution from long-range European sources
Vredepeel	Agricultural activities, livestock, and European PM transported over long-range

sources (which are discussed in more detail in the following paragraphs), thereby making it possible to collect particulate matter with distinctly different chemical composition, a highly desirable feature for toxicity studies targeting specific PM compounds. The sampling inlets of MOUDI and HEADS were connected through the holes to outside of trailer and located on the opposite end of the blower venting system in order to avoid sampling interference from the blower exhaust. Also, shower caps were installed to cover MOUDI and HEADS sampling ports to prevent the rain droplets entering samplers in rainy days.

From June 1 to July 2, 1999, the HCPSC trailer was transported between two locations in Utrecht (REMU and Koningsbruggen). Sampling each weekday started 3:00 p.m. in the afternoon and ended at 11:00 a.m. of the following morning. On weekends, time integrated samples were obtained from 3:00 p.m. on Friday afternoon to 11:00 a.m. on Monday morning. Sampling duration was chosen such that it would cover the emission of traffic rush hours and time needed for dispersion. Both REMU and Koningsbruggen are locations affected by Utrecht city background aerosol emissions as well as by emissions from nearby heavy freeway-traffic (diesel exhaust). REMU is also influenced by light industrial activities in the west of Utrecht.

From July 2 to July 26, the HCPSC was transported three other sites in the Netherlands: Amsterdam (RCA), Vredepeel and De Zilk every other day in July. These sites were also sites of a major source apportionment study by RIVM. The city site in Amsterdam represented an area dominated by dense traffic PM emissions. The main PM sources in Vredepeel are agricultural activities and livestock as well as European PM transported over long ranges. Most of the time in the Netherlands, the wind direction is west or southwest. Therefore, De Zilk serves as a background coastal area with smaller contribution from long-range European sources compared to Vredepeel. Sampling started at 4:00 p.m. and ended at 10:00 a.m. of the following morning (18 h), during weekdays and from Friday 4 p.m. until Monday 10:00 a.m. on weekends. Daily sampling decreased from 20 to 18 h due to the time needed for trailer transportation between locations and sample preparation. A total of 40 field comparisons between HCPSC and MOUDI were conducted. The HEADS was only used in 15 of these field tests to assess losses of particulate nitrate from both samplers. Although not described in this paper, the PUF substrates and Teflon sheets of the HCPSC were also analyzed by means of inductively coupled plasma mass spectroscopy (ICPMS) in order to determine the elemental composition of the collected particles. Results from this analysis are presented in a separate manuscript that describes *in vitro* toxicity studies using these particles (Cassee, Sioutas, Chang & Kleinman, 2000).

3. Results and discussion

3.1. Evaluation of blank content of impaction substrates

The chloride, nitrate and sulfate content of blank 20×25.4 cm PTFE Teflon and quartz filter sheets, as well as polyurethane foams used for coarse and fine PM collection are shown in Table 2. The analysis of blanks indicated very low inorganic ion levels for all the substrates used in this study. In a typical 18-h sampling period, the surface density of the particulate deposit was on the order of $1\text{--}3 \text{ mg cm}^{-2}$, thus three orders of magnitude higher than the blank content. Due to the low chemical background (Table 2) and high recovery for toxicity extraction (Salonen et al., 1999),

Table 2

Blank content of chloride, nitrate and sulfate for different substrate materials. Data are in μg of particles per cm^2 of substrate surface area and correspond to substrates extracted with 14 ml deionized water and 3 ml of ethanol

	Chloride	Nitrate	Sulfate
Ion chromatography limit of detection (LOD)	0.52	0.30	0.47
PTFE sheet	< LOD	< LOD	< LOD
Quartz filter	< LOD	< LOD	< LOD
Polyurethane foam (PUF)	0.91	< LOD	0.72

PUF was chosen as the optimum impaction substrate for the 2.5–10 μm and the 0.15–2.5 μm stages of the HCPSC. Other substrates (e.g., glass fiber, quartz, Fluoropore™) can be used for particle collection, as they also result in high collection efficiency and high particle retention (Sioutas et al., 1997; Chang et al., 1999).

3.2. Evaluation of HCPSC

The results from the field evaluation of the HCPSC are shown in and Figs. 3–8, along with the linear regression lines and correlation coefficients, and summarized in Tables 3 and 4. As the first stage of the HCPSC was designed to have a cutpoint at 2.5 μm (which is intermediate to the 1.8 and 3.2 μm cutpoints of the corresponding MOUDI stages), the mass and ionic species concentrations determined with the MOUDI in the 1.8–3.2 μm size range were equally divided between coarse and fine modes in order to facilitate the HCPSC–MOUDI comparison. This assumes that 2.5 μm is the mass median diameter of the 1.8–3.2 μm range. The validity of this assumption is not particularly crucial, considering that the fraction of mass and ionic species concentrations in the 1.8–3.2 μm size range was generally small (i.e., less than 10%) in virtually all of the experiments. In general, measurable nitrate and sulfate levels were found in all three particle modes, whereas chloride levels were almost exclusively associated with the coarse PM mode.

Table 4 presents a summary of the MOUDI-to-HCPSC concentration ratios based on mass, chloride, nitrate, and sulfate and classified in coarse, fine and ultrafine modes. Figs. 3a–d show the coarse PM mass, chloride, sulfate and nitrate concentrations of the HCPSC plotted against those measured by means of the MOUDI. Very good overall agreement was obtained between the mass, chloride, nitrate and sulfate concentrations determined by the HCPSC and MOUDI with average ratios of $1.06 (\pm 0.22)$, $1.04 (\pm 0.26)$, $0.95 (\pm 0.29)$, and $1.07 (\pm 0.26)$, respectively (Table 4). Moreover, Figs. 3a–d indicate that the mass, chloride, nitrate and sulfate concentrations determined by means of the HCPSC and MOUDI were highly correlated, with correlation coefficients (R^2) of 0.84, 0.97, 0.90 and 0.88, respectively, for coarse PM mass, chloride, nitrate and sulfate.

The comparison between HCPSC and MOUDI based on fine particulate sulfate and nitrate concentrations is shown in Figs. 4a, b and Table 4. The results in Fig. 4a indicate excellent agreement between the MOUDI and HCPSC nitrate concentrations, with the average HCPSC-to-MOUDI nitrate concentrations being $1.02 (\pm 0.21)$. MOUDI and HCPSC nitrate concentrations are also highly correlated ($R^2 = 0.90$). However, the results of Fig. 4b and Table 4 indicate

that the average sulfate concentrations measured by the HCPSC are about 13% lower than those measured by the MOUDI for 0.15–2.5 μm particles. This discrepancy could be due to a possible difference in the 50% cutpoints between the MOUDI and the HCPSCS as well as to the imperfect collection characteristics of rectangular geometry impactors (such as the HCPSC) compared to round-nozzle impactors (i.e., MOUDI). The former explanation is unlikely, as previous experimental characterization of the slit impactor of the HCPSC (Sioutas et al., 1997) indicated that the

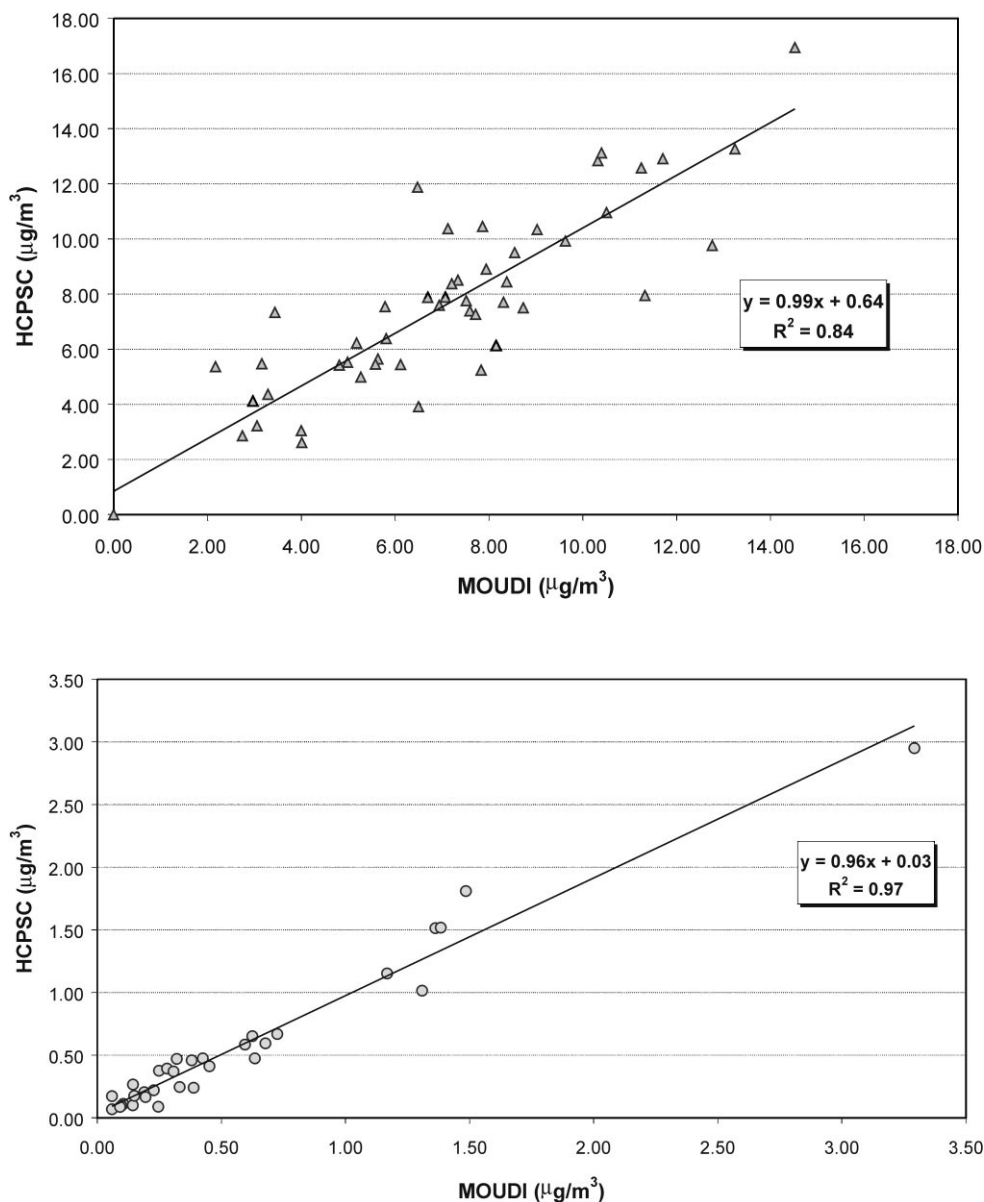


Fig. 3. Comparisons of mass, chloride, nitrate and sulfate concentrations between HCPSC and MOUDI in coarse mode.

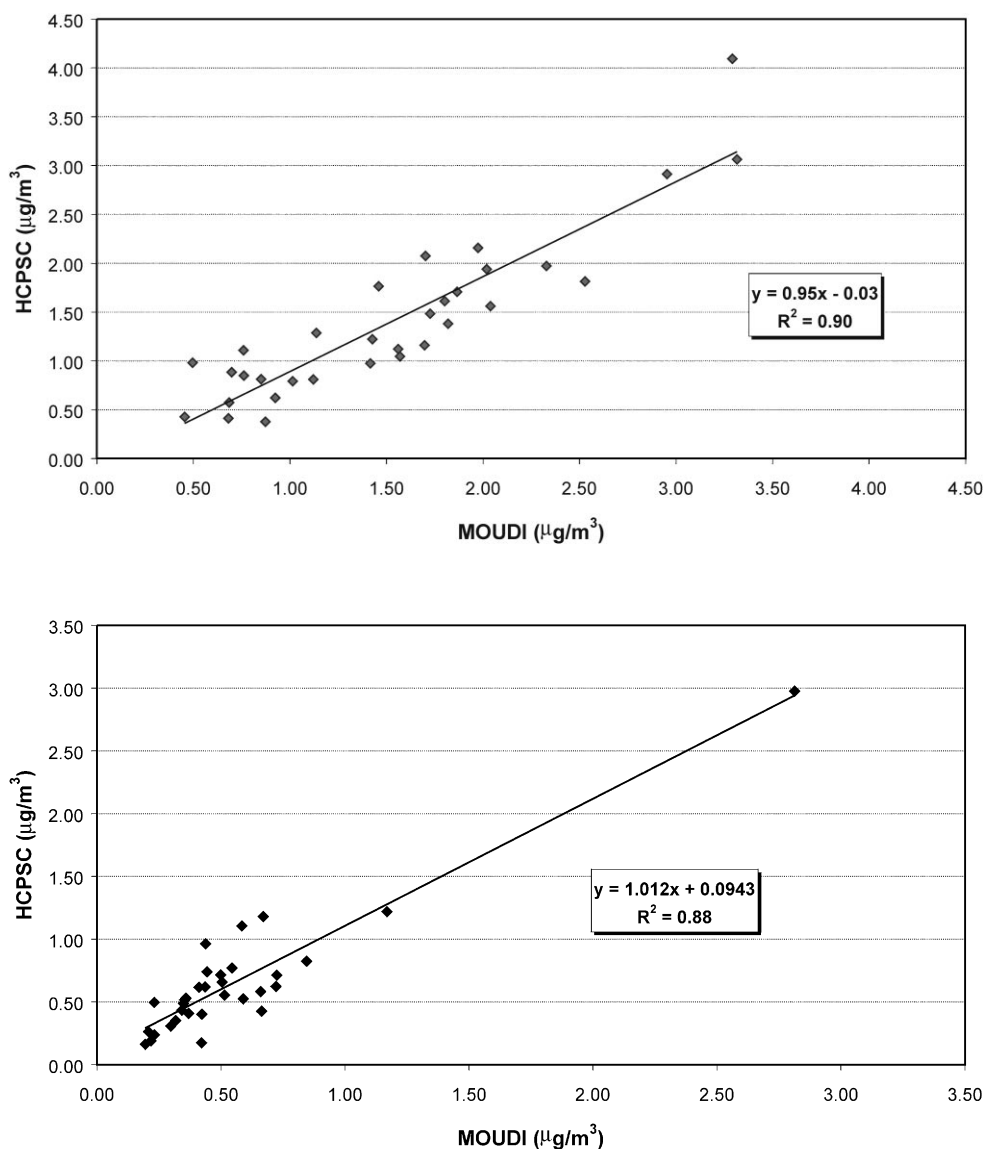


Fig. 3 (continued).

50% cutpoint was about $0.15\ \mu\text{m}$. The aforementioned study, however, showed that the collection efficiency curve of the slit impactor of the HCPSC is not as sharp as that of a round nozzle impactor. While the 50% cutpoint is around $0.15\ \mu\text{m}$ in aerodynamic diameter, particles in the $0.2\text{--}0.3\ \mu\text{m}$ range are collected with an average efficiency of 75–80%. By comparison, particles in the size range $0.2\text{--}0.3\ \mu\text{m}$ range are collected with virtually 100% efficiency, according to the performance evaluation of the MOUDI described by Marple, Rubow and Behm (1991). The excellent agreement between MOUDI and HCPSC obtained for nitrate concentrations is

Table 3

Range of total mass and (ionic) species concentrations ($\mu\text{g m}^{-3}$) levels for each size range during HCPSC evaluation (from April 29 to July 26, 1999)

Mode	Mass	Chloride	Nitrate	Sulfate
Coarse	2.6–17.0	0.1–2.95	0.38–4.10	0.17–2.98
Fine	4.35–33.1 ^a	0.08–2.18	0.9–8.5	1.14–9.54
Ultrafine	0.49–6.42 ^a	0.04–1.28	0.04–3.34	0.24–5.75

^aGravimetric measurement is not available in HCPSC fine and ultrafine mode. Based on MOUDI data only.

Table 4

Summary of the ratios (Mean \pm S.D.)^a of HCPSC-to-MOUDI species concentrations based on mass, chloride, nitrate, and sulfate in coarse, fine and ultrafine PM modes

	Mass	Chloride	Sulfate	Nitrate
Coarse	1.06 (± 0.22)	1.04 (± 0.26)	1.07 (± 0.26)	0.95 (± 0.29)
Fine	NA ^{b,c}	NA ^d	0.87 (± 0.19)	1.02 (± 0.21)
Ultrafine	NA ^{b,c}	NA ^d	2.05 (± 0.85)	5.27 (± 4.85)

^aAverage ratios (Mean \pm S.D.) of 40 field tests.

^bAlso weighing is unavailable due to static interference with the microbalance.

^cWeighing is unavailable due to the substrate dimension.

^dLow chloride content, close to instrument detection limit.

undoubtedly due to the generally small fraction of nitrate associated with particles below $0.2 \mu\text{m}$ in the Netherlands (Ten Brink, Kruis, Kos & Berner, 1997). As the contribution of $0.15\text{--}0.3 \mu\text{m}$ particles to the overall accumulation mode PM sulfate is non-negligible, MOUDI concentrations will be 5–15% higher to those measured by the HCPSC, depending on the particulate sulfate size distribution.

These results also imply that, on the average, about 13% of accumulation mode particles will be carried over to the after-filter of the HCPSC, which is collecting ultrafine particles. Depending on the relative contributions of accumulation and ultrafine PM modes to the overall mass, this particle carry-over may affect significantly the HCPSC–MOUDI comparisons based on ultrafine PM concentrations, which are summarized in Table 4 and Figs. 5a and b. HCPSC sulfate and nitrate concentrations are considerably higher than those determined by the MOUDI. Our field tests indicated that the fraction of PM-2.5 sulfate (by mass) found in the ultrafine mode varied in the range of 5–15%. Assuming that, on the average, about 10% of the accumulation mode particles are collected by the after-filter of the HCPSC, ultrafine sulfate concentrations measured by the HCPSC would be approximately higher than those of the MOUDI by about 70–100%. This is confirmed by the results shown in Fig. 5a and Table 4, in which the average HCPSC sulfate concentrations for ultrafine PM are approximately two times higher than to those of the MOUDI. The very high correlation ($R^2 = 0.90$) between the MOUDI and HCPSC data also indicates that the discrepancy between the two samplers for ultrafine particulate sulfate is systematic.

Ultrafine PM concentrations based on nitrate measured by means of the HCPSC and MOUDI are shown in Fig. 5b. On the average, the HCPSC nitrate concentrations are higher by a factor of about 5 compared to those of the MOUDI (Table 4). Furthermore, the MOUDI and HCPSC

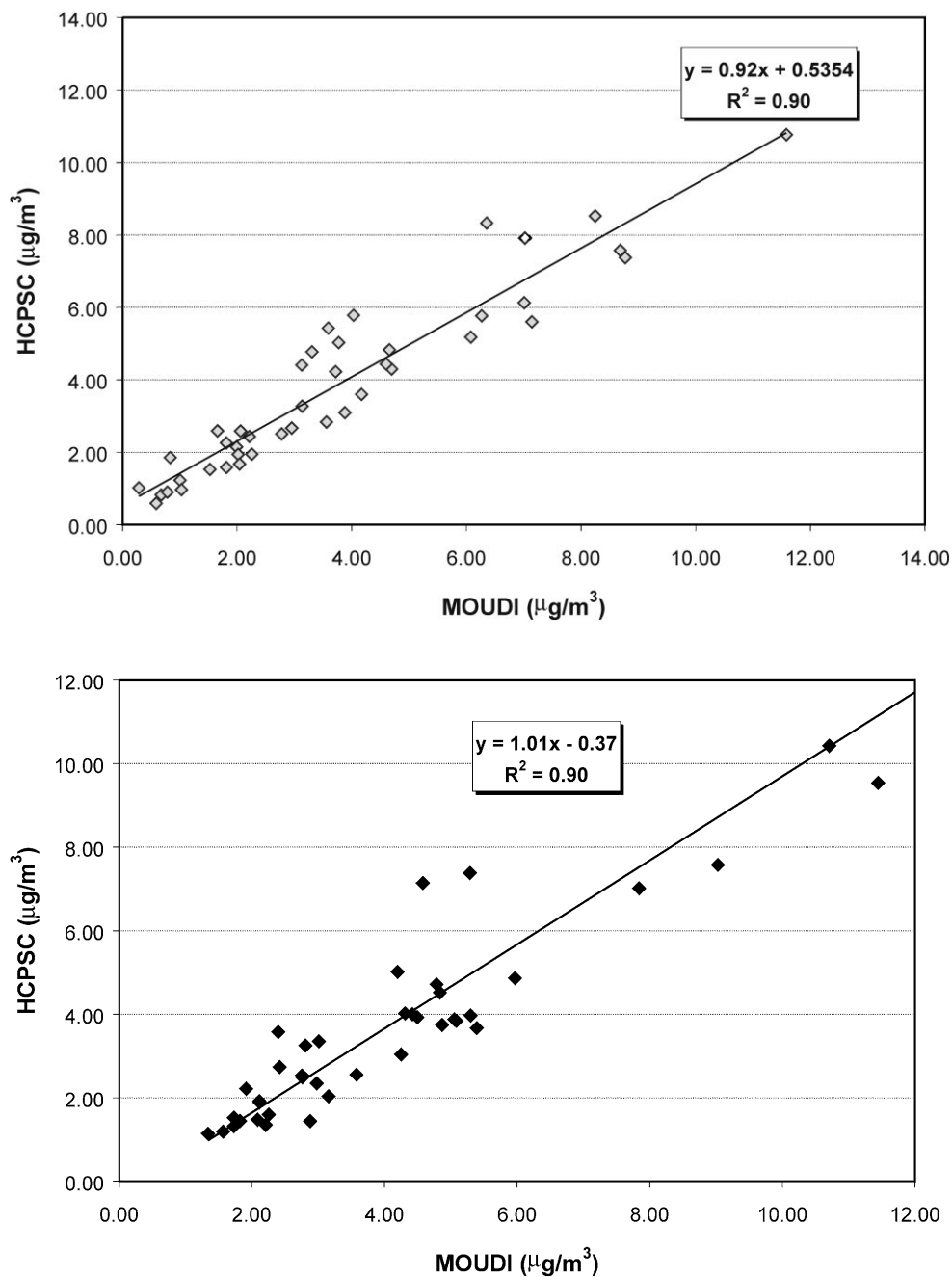


Fig. 4. Comparisons of nitrate and sulfate concentrations between HCPSC and MOUDI in fine mode.

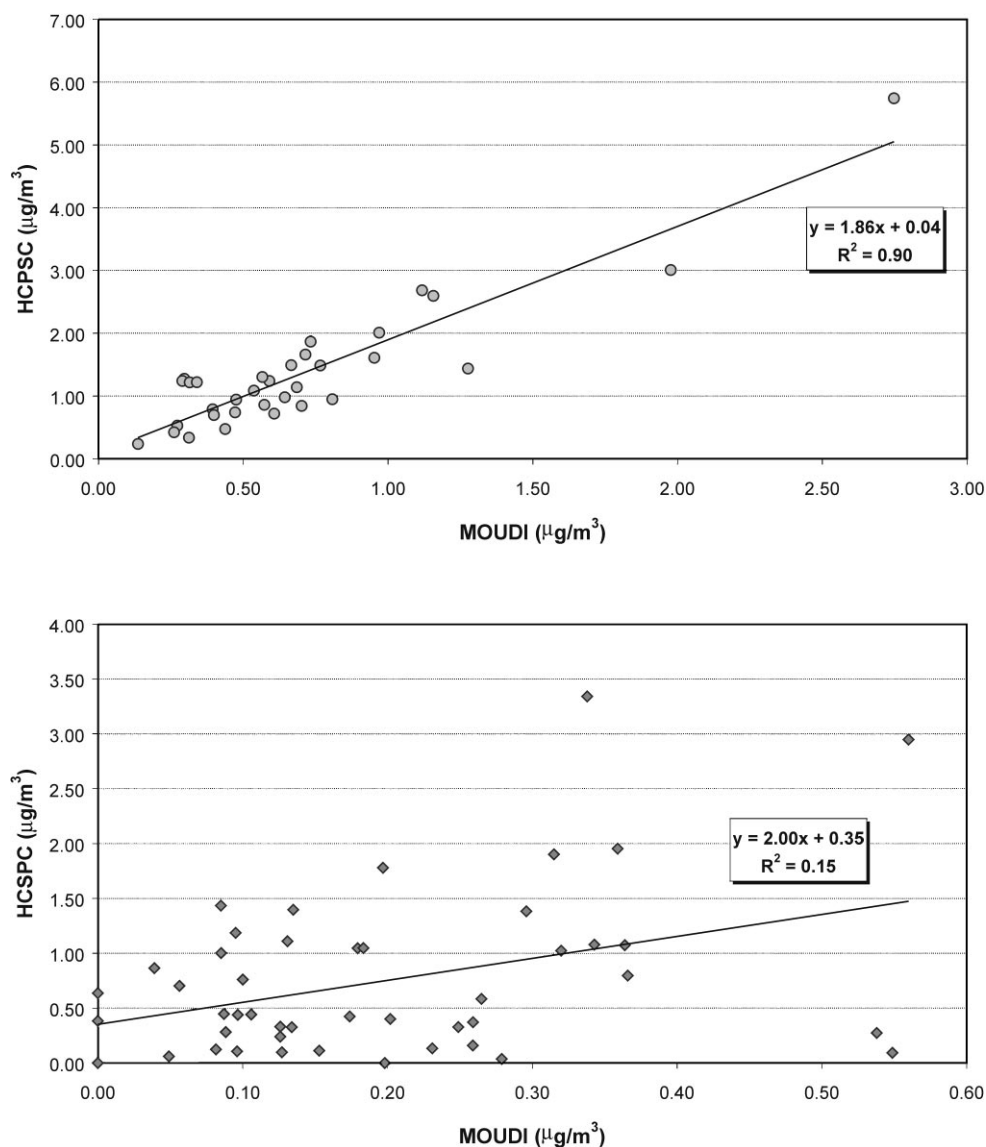


Fig. 5. Comparisons of nitrate and sulfate concentrations between HCPSC and MOUDI in ultrafine mode.

concentrations are poorly correlated ($R^2 = 0.15$). The large discrepancies and poor correlation between the ultrafine nitrate concentrations determined by the HCPSC and MOUDI cannot be attributed only to the relative differences in the cutpoint characteristics between rectangular and round geometry impactors. This is because, as it will be discussed in the following section, the nitrate concentrations determined by either sampler can be considerably biased due to loss of volatile ammonium nitrate from either MOUDI or HCPSC filter collecting ultrafine PM.

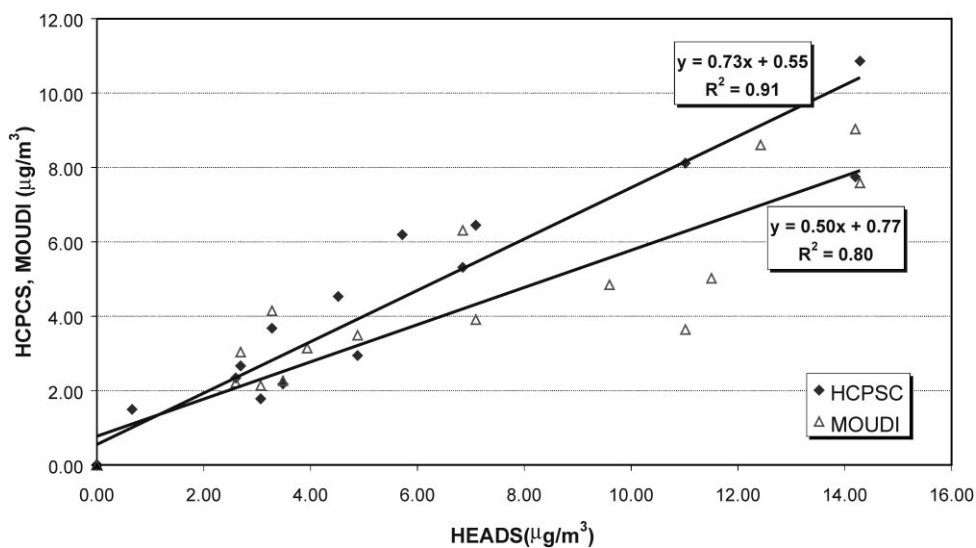


Fig. 6. Comparison of total PM-2.5 nitrate concentrations in HCPSC and MOUDI to HEADS.

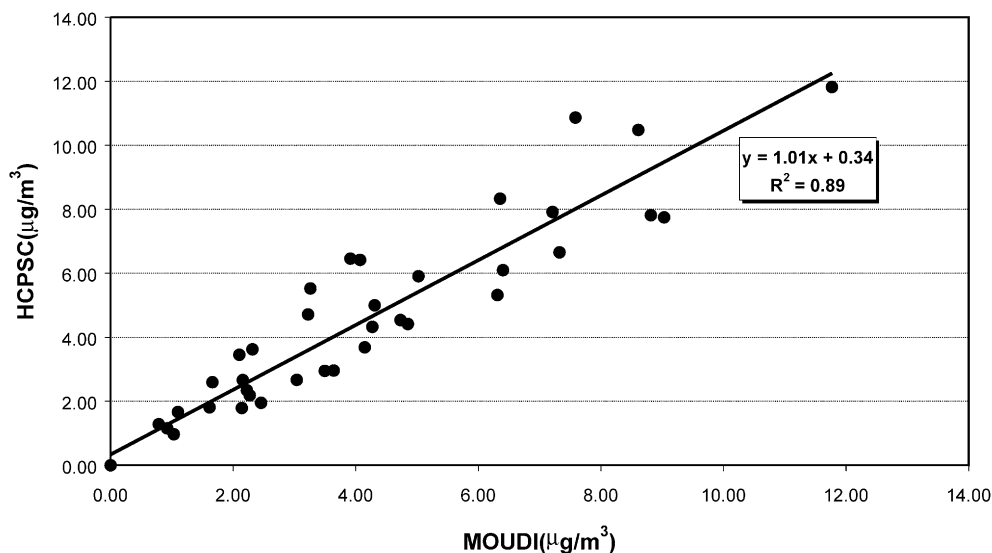


Fig. 7. Comparisons of total PM-2.5 nitrate concentrations between HCPSC and MOUDI.

3.3. Evaluation of nitrate volatilization and sampling artifacts

An important consideration regarding the performance of any sampler is the ability to sample volatile or semi-volatile PM constituents without substantial losses during sampling and collection. To address this issue, the concentrations of particulate nitrate determined by the HCPSC and MOUDI were compared to those measured by means of the Harvard/EPA Annular Denuder System (HEADS).

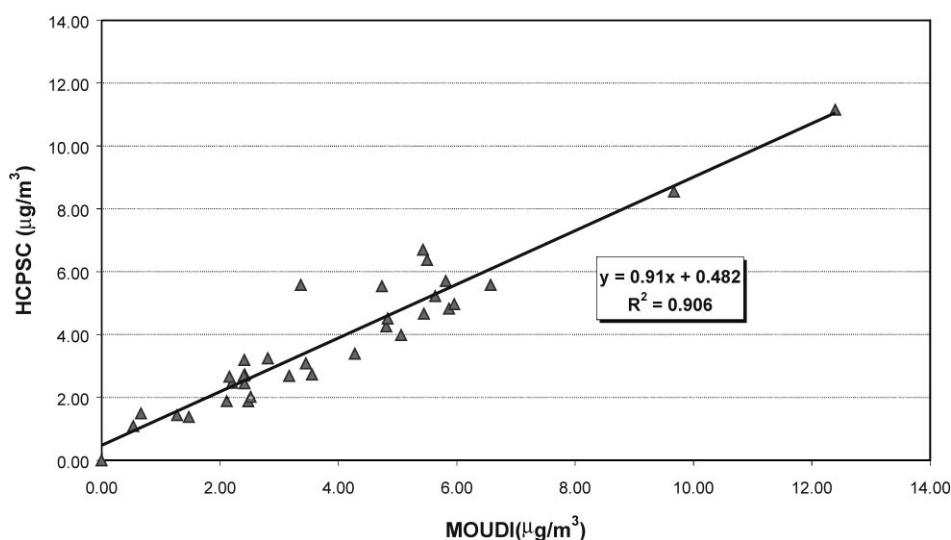


Fig. 8. Comparisons of total PM-2.5 sulfate concentrations between HCPSC and MOUDI.

Table 5

Ratios of the PM-2.5 nitrate and sulfate concentrations obtained using the MOUDI, HCPSC, and HEADS^a

	Nitrate	Sulfate
MOUDI/HEADS	0.71 (± 0.23) ^b	1.02 (± 0.11) ^b
HCPSC/HEADS	0.80 (± 0.20) ^b	0.99 (± 0.16) ^b
PTFE filters/HEADS ^d	0.46 (± 0.24) ^b	1.00
HCPSC/MOUDI	1.16 (± 0.29) ^c	0.99 (± 0.20) ^c

^a Average ratios (Mean \pm S.D.).

^b Total numbers of tests: 15.

^c Total numbers of tests: 40.

^d Ratio of the Teflon filter to the total HEADS concentration.

Results from the particulate nitrate comparison between the HCPSC and the HEADS as well as between the MOUDI and HEADS are shown in Fig. 6 and Table 5. The average HCPSC-to-HEADS and MOUDI-to-HEADS nitrate concentration ratios were $0.80 (\pm 0.20)$ and $0.71 (\pm 0.23)$, respectively. Higher correlation was observed between the HCPSC and HEADS concentrations ($R^2 = 0.90$) than between the HEADS and MOUDI concentrations ($R^2 = 0.77$). Direct comparison between the total PM-2.5 nitrate concentrations (i.e., the sum of fine plus ultrafine particulate nitrate) determined with the HCPSC and MOUDI (Fig. 7) showed that the HCPSC nitrate concentrations were higher to those of the MOUDI on the average by 16% (Table 5). These results suggest that the sampling efficiency of the HCPSC for particulate nitrate is higher than that of the MOUDI, mainly due to the higher particle loading per unit collection surface area of the HCPSC.

In the HCPSC, accumulation mode particles (accounting for over 90% of the total PM-2.5 nitrate) are collected at 850 l min^{-1} on a total surface area of 14 cm^2 . By comparison, fine particles are collected at 30 l min^{-1} on a total surface area of about 13 cm^2 (i.e. exposed surface area of a 4.7 cm filter) in the MOUDI.

Previous investigations on losses of ammonium nitrate from impactor and Teflon filter substrates showed that these losses increase significantly with increasing exposed surface area per unit mass of the deposit (Chang et al., 2000). The overall excellent agreement between HCPSC and MOUDI based on non-volatile total PM-2.5 sulfate concentrations (shown in Fig. 8) provides further corroboration to the hypothesis that the systematically higher nitrate concentrations measured by the HCPSC are due to higher nitrate losses of the MOUDI. The excellent overall agreement between the fine mode nitrate concentrations of the HCPSC and MOUDI suggests that the majority of nitrate losses in MOUDI must be associated with PM in the ultrafine mode. This could be due to the higher face velocity of the MOUDI filter collecting ultrafine particles (e.g., 58 cm s^{-1}), compared to that of the HCPSC (e.g., 28 cm s^{-1}). The higher face velocity in MOUDI filter would result in a higher pressure drop across the filter and thus would increase the rate of evaporation of particulate nitrate from the filter (Zhang & McMurry, 1987; Chang et al., 2000). In general, losses of particulate ammonium nitrate from impactor and filter substrates increase with ambient temperature, decrease with increasing relative humidity and decrease with increasing values of ratio of equilibrium particulate-to-gas phase nitrate concentrations (Zhang & McMurry, 1992; Chang et al., 2000). As the values of these parameters varied substantially over the 3-month sampling period, nitrate losses from the MOUDI substrates are not expected to be consistent (e.g., the same in each tests), but vary rather randomly. The random nature of these losses explains the low correlation coefficients obtained between the ultrafine nitrate concentrations of HCPSC and MOUDI as well as the large standard deviations of the HCPSC-to-MOUDI concentration ratios (Table 5).

Although systematic evaluation of sampling artifacts from impactor and filter substrates was beyond the scope of this study, of particular note are the excessive nitrate losses from Teflon filters, which were observed by comparing the nitrate concentrations measured by the Teflon filter of the HEADS to the total HEADS nitrate concentrations. The average sampling efficiency of the Teflon filters was $0.46 (\pm 0.24)$, thereby implying that more than 55% of PM-2.5 nitrate was lost from the Teflon filter during sampling. These findings are in good agreement with previous theoretical (Zhang & McMurry, 1987) or experimental (Zhang & McMurry, 1992; Sioutas et al., 1997) studies, which demonstrated that nitrate losses in impactors are generally lower than those in filter samplers. Evaporative losses from filters are considered to be more serious than those from impactor samplers due to higher deposited particle surface area per mass exposed to airflow in filter samplers than in impactors.

4. Summary and conclusions

A mobile high-capacity particle size classifier (HCPSC) has been developed and evaluated in field experiments conducted in the Netherlands from May to August 1999. The HCPSC samples at 850 l min^{-1} and classifies ambient particles at three size groups: coarse, fine and ultrafine modes. Particles in coarse and fine modes are collected in a small surface area of 14 cm^2 and can be

extracted with small volume of solvent (5–10 ml). Ultrafine particles are collected on 20×25 cm quartz or Teflon filters. Field tests showed that mass, chloride, nitrate and sulfate concentration in the coarse mode (10– $2.5 \mu\text{m}$) measured by the HCPSC and a collocated Micro-Orifice Uniform Deposited Impactor (MOUDI) were in very good agreement (within 10% or less). Comparison between fine mode sulfate concentrations obtained with the HCPSC and MOUDI indicated that approximately 10–15% of fine mode particles are carried over to the ultrafine mode due to the imperfect collection efficiency characteristics of a rectangular geometry impactor compared to a round nozzle impactor. Comparisons between the PM-2.5 nitrate concentrations obtained with the HCPSC and MOUDI and those with a collocated Harvard/EPA Annular Denuder Sampler (HEADS) indicated that the average nitrate collection efficiencies of the HCPSC and MOUDI are approximately 80 and 70%, respectively. Both samplers have substantially higher nitrate sampling efficiencies than Teflon filters, in which more than 50% of particulate nitrate (on the average) is lost due to volatilization during sampling.

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